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Preliminary Study of Steels Corrosion Phenomena in Liquid Lead-Bismuth using Molecular Dynamics Methods

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Abstract

One of the prospective coolant material which can be used in the forth generation nuclear reactor is a liquid lead-bismuth. This coolant has inherent safety capability, economical, and able to burn their own nuclear waste. The problem of using this coolant is corrosion phenomena of steel occurred in the interaction with liquid lead-bismuth especially at high temperatures. Corrosion in this study is assumed as diffusion phenomena of leads or bismuths into the surface of steel. This phenomenon have been studied by molecular dynamic methods. As the first step to this investigation, the molecular dynamic program called Moldy has been used to simulate pure iron and lead system. The molecular dynamic simulation result of pure Fe system at 0 K showed that the peaks positions of radial distribution function is in a good agreement with the result from experiment. The deviation of the peaks position resulted from simulation and experiment is about 0.5%. The simulation result of Pb system showed no significant different with the result from experiment. The simulation also shows the broadening of the curves of radial distribution function and lowering the intensity at high temperature. These results indicate that the atomic positions of the system are distributed randomly.

Keywords: *Molecular dynamic, Lennard-Jones potential, liquid lead-bismuth, corrosion, radial distribution function.*

1. Introduction

Liquid lead-bismuth (Pb-Bi) is a candidate coolant in the forth generation nuclear reactor. The application of liquid lead-bismuth in this reactor show inherent safety capability, economical, and able to burn their own nuclear waste. Some of the properties of lead-bismuth are its melting point at 123.5 °C and boiling point at 1670 °C with volume change upon solidification at about 1.5%. The other properties of this material are inert with water and air. The problem in the application of liquid lead-bismuth as coolant in nuclear reactor is corrosion of structural material like stainless steel occurred especially at high temperatures[5)].

Many researchers have studied this problem experimentally in order to understand the corrosion phenomena of steel in contact with this liquid metal. In this study, the simulation has been done using molecular dynamics technique. The corrosion in this simulation is assumed as a phenomenon of penetration of lead or bismuth atoms into stainless steels.

A molecular dynamics simulation is a technique that solves the equation of motion for a system of molecules or atoms that interact with each other through interatomic potential[1)]. In this simulation, positions and velocities of molecules were calculated as a function of time-step. Result of this calculation can be processed based on the statistical mechanics to get macroscopic properties of materials such as temperature, radial distribution function, mean square displacement etc.

In this computer experiment, we tried to use a Moldy pocket as a free source code of molecular dynamic program[6)]. The Moldy pocket can be used in the Linux and window system and written in C language. Linux system is used in our study. The source of Moldy consists of 31 source files amounting to 167 functions and 9000 lines of codes.

As the preliminary study of corrosion phenomena of steel in liquid Pb-Bi, we tried to simulate the pure iron (Fe) and lead (Pb) system individually. In this study, we want to know the capability of Moldy code especially in order to identify the phase system of Fe and Pb system at some temperatures. The Fe and Pb systems are used in this simulation because both materials will be used in the next study with some modification.

2. Theory

One way to understand the behavior of a many particle system is to begin from the known intermolecular interactions and do a computer simulation of its dynamic. This approach is known as the molecular dynamic method. The first step to do this simulation is to specify the model we wish to simulate. In this simulation, we assume that dynamics can be treated classically and that the molecules or atoms are spherical and chemically inert. The forces between any pair of molecules are also assumed depends only on the distance between them. The total energy U is a sum of two particle interaction:

$$U = u(r_{12}) + u(r_{13}) + \ldots + u(r_{23}) + \ldots = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij}) \quad (1)$$

where $u(r_{ij})$ depends only on the magnitude of the distance $\boldsymbol{r}_{\mathrm{ij}}$ between particles i and j.

The interatomic potential between atoms is assumed to follow pairwise additive intermolecular potential called Lennard-Jones potential:

$$u_{ij}^{LJ}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} + \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \quad (2)$$

where u_{ij}^{LJ} is the Lennard-Jones potential between the two atoms i and j, r_{ij} the interatomic distance, ϵ the potential depth and σ the potential parameter. . The Lennard-Jones potential is characterized by a strong repulsive force at very short range and a weak attractive force at intermediate range. Therefore usually the potential used in the simulation is truncated at radius cutoff r_{cut} and the equation was determined by:

$$u_{ij} = \begin{cases} u_{ij}^{LJ} & ; r_{ij} \le r_{cut} \\ 0 & ; r_{ij} > r_{cut} \end{cases} \quad (3)$$

A common choice for r_{cut} is 2.5σ, at which only about 1.6% of the minimum energy. If the value of $r_{ij} = r_{cut}$, atom j makes only a small contribution to the force on atom i.

The gradient of potential in equation (2) is then used to determine the force that atom j exert on atom i:

$$\mathbf{F}_{ij} = -\nabla u_{ij} \quad (4)$$

which is then summed over all pairs and give a net force on atom i:

$$m\ddot{\mathbf{r}} = \mathbf{F}_i = \sum_{\substack{j=1 \\ j \ne i}}^{N} \mathbf{F}_{ij} \quad (5)$$

where m is atomic mass.

The equation (5) can be solved numerically by finite different method. In this study we used Beeman algorithm. The Beeman equation may be written as follow:

$$\begin{aligned}
&i.\ r(t+\delta t) = r(t) + \delta t\,\dot{r}(t) + \frac{\delta t^2}{6}\left[4\ddot{r}(t) - \ddot{r}(t-\delta t)\right] \\
&ii.\ \dot{r}^{(p)}(t+\delta t) = \dot{r}(t) + \frac{\delta t}{2}\left[3\ddot{r}(t) - \ddot{r}(t-\delta t)\right] \\
&iii.\ r(t+\delta t) = F\left(\left\{\ r_i(t+\delta t), \dot{r}_i^{(p)}(t+\delta t)\right\},\ \ i = 1 \ldots n\right) \\
&iv.\ \dot{r}^{(c)}(t+\delta t) = \dot{r}(t+\delta t) + \frac{\delta t}{6}\left[2\ddot{r}(t+\delta t) + 5\ddot{r}(t) - \ddot{r}(t+\delta t)\right] \\
&v.\ replace\ \ \dot{r}^{(p)}\ with\ \dot{r}^{(c)}\ and\ \ goto\ \ iii.
\end{aligned} \quad (6)$$

where $\dot{r}^{(p)}$ and $\dot{r}^{(c)}$ represent predicted and corrected velocities respectively.

The above equations generate the positions and velocities of particles as a function of time step. Therefore to measure an observable quantity in molecular dynamic simulation, the observable should be expressed as a function of the position and velocities of the particles in the system. The relation between instantaneous temperature with the velocities is as follow[3)]:

$$T(t) = \sum_{i=1}^{N} \frac{m_i \dot{r}_i^2(t)}{k_B N_f} \quad (7)$$

where, k_B is the Boltzmann constant, N_f is the number of degrees of freedom and for a system of N particles $N_f = 3N + 3$.. Temperature of the system can be set either by scaling method or Nose-Hoover thermostat method. In this paper, we used the Nose-Hoover thermostat.

The other important observable quantity is the radial distribution function equation which can be written as follow:

$$g(r) = \frac{\langle N(r, \Delta r) \rangle}{\frac{1}{2} N\rho V(r, \Delta r)} \quad (8)$$

where ρ is the density of atoms (Haile, 1997). The radial distribution function $g(r)$ measures how atoms organize themselves around another. It is proportional to the probability of finding two atoms separated by distance $r \pm \Delta r$.. The behavior of $g(r)$ can be used to help identifying the phase of simulated system. For crystalline solids, the curve of $g(r)$ contains deeper valleys and higher narrower peaks than does $g(r)$ for fluids.

The simulation requires the initial condition of positions and velocities of all atoms involved in the system. The unit cell of the systems can be extended periodically in three dimensions with the equation:

$$\vec{r} = \vec{r}_{uc} + n_x \vec{a} + n_y \vec{b} + n_z \vec{c} \quad (9)$$

where $\vec{r}_{uc}$ is the vector position of unit cell, n_x, n_y, n_z are the number of cell in the x,y,z directions $\vec{a}, \vec{b}$ and $\vec{c}$ are the unit vector in the Cartesian coordinates.

3. Methodology

The initial positions of Fe was developed based on the BCC (Body Center Cubic) structure with lattice parameter 2.8665 Å and Pb atoms are determined to fill the FCC (Face Center Cubic) structure with lattice parameter 4.9508 Å[7)]. The Fe structure have two atoms in every unit cell, therefore the initial positions of the Fe system can be made by replicating of these two coordinates using equation (9) in three dimension. In this simulation the system Fe is developed by 2000 atoms in which the n_x, n_y and n_z is equal to 10.

The system of FCC structure has four atoms in every unit cell. Therefore the initial configuration of Pb can be made by four initial coordinate's atom. These initial coordinates are (0,0,0), (0,1/2,1/2), (1/2,1/2,0) and (1/2,0,1/2). The Pb system in this simulation is developed by 864 atoms with the number cell n_x, n_y, n_z is equal to 6.

The Lennard-Jones potential parameters of Fe-Fe, Pb-Pb and Bi-Bi atoms had been derived by fitting data available in the literature[3)] with the equation (2). The results are shown in Table 1.

Table 1. Lennard-Jones parameters used in this study.

No	Element	ε (eV)	σ (Å)
1	Fe-Fe	-0.62	2.26
2	Pb-Pb	-0.125	2.75
3	Bi-Bi	-0.075	2.8

The simulations have been done at temperatures 0 K to 1809 K for Fe system and for Pb system at temperatures 0 K to 773 K. Both systems have been simulated by 20000 steps with time-step 0.0005 picosecond. In these simulations the temperatures were controlled by Nose-Hoover thermostat.

4. Result and Discussion

The atomic position of Fe at 0 K after 20000 step molecular dynamic simulation with time-step 0.0005 picosecond are shown in Figure 1. The configuration of Fe atoms occupy the BCC lattice structure regularly which means that the Fe system was frozen in the solid phase.

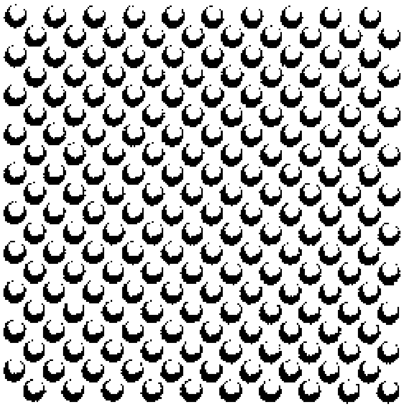


Figure 1. Atomic position of Fe after molecular dynamic simulation at 0 K.

Figure 2 shows the radial distribution function of the Fe system at 0 K. The radial distribution $g(r)$ as a function of the distance between atoms results the curves which forms of a sequence of delta symbols. Materials which have a BCC structure are usually separated by $\frac{1}{2}\sqrt{3}a$, $\sqrt{2}a$, $2a$ distance of atomics pairs[1,7)], where a is a lattice parameter. The comparison between the data result from experiment and molecular dynamic simulation are shown in Table 2. The deviation of the peaks position result from simulation and experiment is about 0.5%.

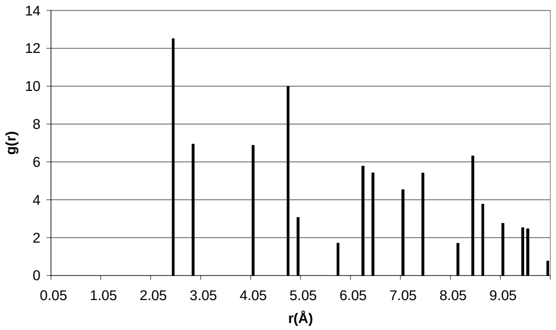


Figure 2. Atomic position of Pb after molecular dynamic simulation at 0 K.

Table 2. Comparison between the data results from simulation and experiment.

Peak number	The distance of atomic pair	Peak position from Experiment (Å)	Peak position from simulation (Å)	Deviation (%)
1	$\frac{1}{2}\sqrt{3}a$	2,48	2,45	1,2
2	a	2,86	2,85	0,3
3	$\sqrt{2}a$	4,04	4,05	0,2
5	$2a$	5,74	5,75	0,2

The radial distribution function of Fe system at some temperatures resulted from simulation are presented in Figure 3. These data showed that at above 0 K the curve did not formed delta symbol anymore. The simulation show the broadening of the curves of the radial distribution function and lowering the intensity at high temperature. This result indicates that the atomic positions of the system are distributed randomly.

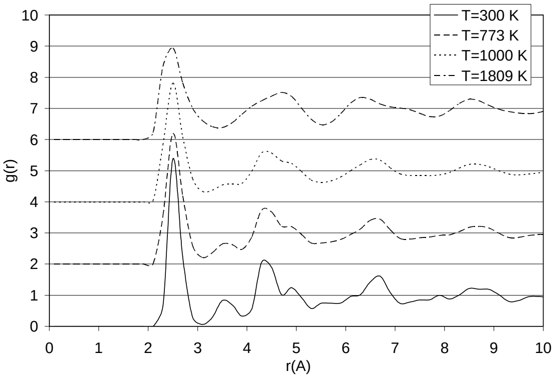


Figure 3. The radial distributions function of Fe system at some temperatures.

The molecular dynamic simulation result of Pb system in two dimensions is shown in Figure 4. All Pb atoms are located at the coordinates of the FCC crystal structure regularly at temperature 0 K. This configuration of Pb atoms indicates that the system in the solid phase.

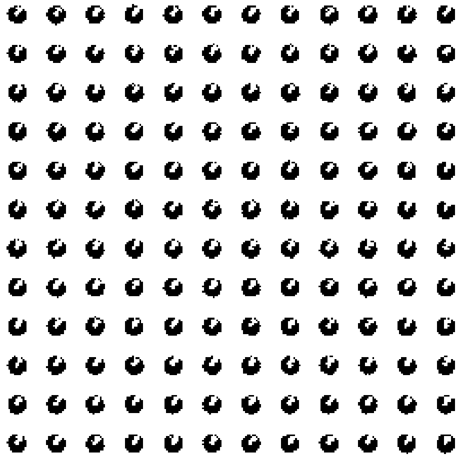


Figure 3. Atomic position of Pb after molecular dynamic simulation at 0 K.

The radial distributions function of the Pb system at 0 K is presented in Figure 5. These result showed that the peak are located at some specific positions of the distance in the form of delta function. The peaks positions of Pb system appear in Figure 5 are caused by FCC lattice structure which has atomics pair separated by $\frac{1}{2}\sqrt{2}a$, a, $\sqrt{2}a$, $2a$ etc. The lattice parameter a in Pb system has a value 4.9508 Å and used to calculate atomics pair separation as the peak position from experiment result. The comparison between the data resulted from molecular dynamic simulation and experiment are shown in Table 3. In this data we assumed that the first and second peak is similar. This comparison showed that no deviation occurred between simulation and experiment result.

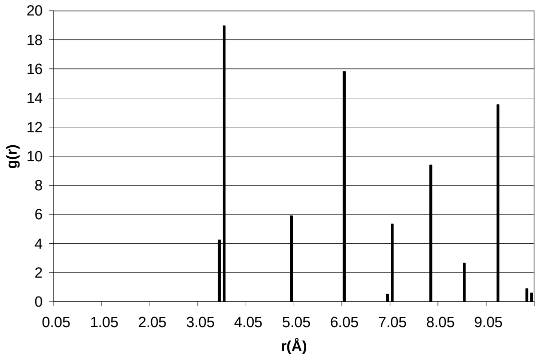


Figure 5. The radial distributions function of Pb system at 0 K.

The radial distribution function of Pb system at temperatures 600 K and 773 K are shown in Figure 6. The simulation shows the broadening of the curves of the radial distribution function and lowering the intensity at high temperature. This data indicated that the atomic positions of Pb were distributed randomly at temperatures 600 K and 773 K. In fact, the melting point of Pb is about 600 K, therefore this data consistent with the experiment. The atomics positions resulted from simulation are also presented in Figure 7. All atoms Pb in both temperatures randomly distributed in three dimension which mean that the systems in the liquid phase.

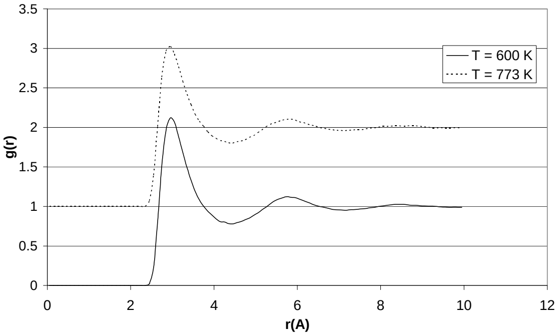
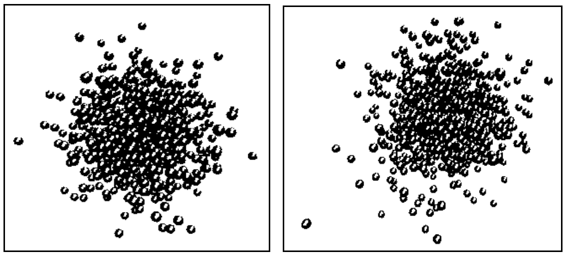


Figure 4. The radial distributions function of Pb system at 600 K and 773 K.



(a) T = 600 K (b) T = 773 K

Figure 7. The atomics position of Pb system at 600 K and 773 K.

Table 3. Comparison between the data result from simulation and experiment of Pb System

Peak number	The distance of atomic pair	Peak position from Experiment (Å)	Peak position from simulation (Å)	Deviation (%)
1, 2	$\frac{1}{2}\sqrt{2}a$	3,5	3,5	0
3	a	4,95	4,95	0
5.6	$\sqrt{2}a$	7,00	7,00	0
10, 11	$2a$	9,9	9,9	0

5. Conclusion and Discussion

The molecular dynamic simulation can be used to study some properties of materials. The radial distribution function of Fe and Pb system result from molecular dynamic simulation can be used to identify the phase of system at some temperatures. The distribution of atomic positions of Fe and Pb system at 0 K are located at coordinates of BCC and FCC crystal structures respectively. The atomic positions of Fe and Pb system are distributed randomly at high temperatures. The knowledge of these properties which is obtained by Moldy code is important information for corrosion study. Therefore in the next experiment, the surface of Fe and Pb system will be contacted and simulated at some temperatures. These simulations are expected can be used to identify the penetration depth of atoms Pb or bismuth into Fe system at high temperatures.

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